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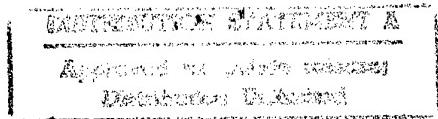
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**Final Report**

**STUDY OF METAL AGGLOMERATION AND COMBUSTION**

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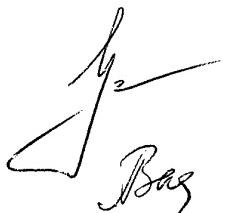
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## ABSTRACT

**Key words:** SRP, Dispersed Oxidizer, Agglomerate, CCP, HDO, Structure, Dispersity

The report contains 45 pages, 31 figures, 7 tables.

The report includes the results of the experimental investigation of the CCP properties close to the burning SRP surface depending on the oxidizer (ammonium perchlorate) dispersity at two levels of pressure. The morphological and chemical properties of agglomerates and HDO particles have been determined in the work.

The obtained data have been analyzed and made it possible to determine more precisely the regularities in the CCP formation. A potential use of propellant structure model in solution of the problem dealing with predicting the CCP parameters close to the burning propellant surface has been shown.

## Abbreviations

- SRP - solid rocket propellant
- CCP - condensed combustion products
- DO - dispersed oxidizer
- AP - ammonium perchlorate
- HMX - octogen
- AN - ammonium nitrate
- ADN - ammonium dinitronitrogen
- HDO - highly dispersed oxide
- CVB - constant volume bomb
- SAM - surface active material
- DBSP- double-base solid propellant;

□

## INTRODUCTION

The presence of metal fuel (MF) in the composition of SRP (Al, as a rule) essentially complicates the propellant burning process. The most vital behavior feature of the given propellant ingredient is the formation of condensed combustion products (CCP). The properties of CCP exert an influence on a number of phenomena which determine the quality of propellant-engine system: burning rate magnitude and losses in the specific thrust momentum, slag deposition in the engine chamber, effect of combustion products on the elements of construction, stability of engine operation. The given properties are formed during the realization of the MF evolution process which is understood as the totality of physical and chemical transformations of Al and its compounds during their presence in the engine chamber.

The evolution process can be divided into two stages depending on where it takes place: in the condensed phase of burning propellant and in the two-phase flow in the combustion chamber. The first stage includes the formation of CCP near the surface of burning propellant. The second stage consists in evolution of CCP in the two-phase flow during its movement.

Studying the MF burning as an ingredient of SRP suggests the investigation of all stages of Al and its compounds "life" in the engine chamber. The present work is devoted to studying the first stage of the evolution process.

## 1. ANALYSIS OF LITERATURE. DEFINING THE INVESTIGATION PURPOSE.

Let us consider in brief the results obtained to date in the investigation of CCP formation near the surface of the burning propellant.

### **1.1. Agglomeration.**

In the phenomena which constitute the first stage of the evolution process the decisive one is the agglomeration - coagulation of condensed products in the surface layer of burning propellant which supplies coagulation products (agglomerates) into the gas phase.

For the first time the agglomeration phenomenon was described in the works of the Institute of Chemical Physics (ICP) of the USSR Academy of Sciences in the early 60s [1]. In the years to follow the practical needs of SRP use had given an impetus to wide investigations of the given phenomenon both in this country and abroad. They comprised getting experimental data, their analysis and development of techniques for predicting the agglomerate characteristics.

These characteristics should include the following:

- parameters determining the chemical composition and structure of agglomerates;
- function of agglomerate size distribution;
- relative quantity of agglomerates in the two phase flow of combustion products.

The purpose of experimental studies was to obtain information on both micro- and macro- regularities of the agglomeration. The micro-regularities will be understood as those which determine the nature of agglomerate formation; the macro-regularities are those which account for relations between agglomerate characteristics and parameters of propellant composition and burning conditions. A set of techniques has been developed to solve these problems [2,4-8,15 and others].

#### A. Structure of agglomerates

There are two concepts of agglomerate structure. First, it is assumed that agglomerates contain some other ingredients (binder or its degradation products, oxidizer) in addition to metal and its oxide. And they may be non-spherical at that [2]. According to the second concept the agglomerates consist of metal and oxide drops [3,5,11-13,15,16].

The mentioned differences observed experimentally are apparently caused by changes in propellant formulations, conditions of burning, and in a number of cases due to inherent characteristics of investigation techniques. Pressure decrease, use of metal in homogeneous propellants [2] contribute to appearance of first type agglomerates. Apparently it can be assumed that for most propellants and a greater range of burning conditions the second type of agglomerates is prevailing. The works [13,15] have shown that the structure of those agglomerates may be different. Its parameters depends on propellant properties and pressure existing during the burning.

#### B. Conditions of agglomerate formation.

At present it is generally assumed that metal particles on the burning propellant surface are retained, may move on the surface and fuse [2,9,10,17,18]. It is assumed that a

necessary condition for fusing is that metal particles reach the temperature of metal melting. The fact that the oxide film doesn't melt is not an obstacle for fusing as it may be broken mechanically [8].

The temperature of burning propellant surface is considered to be essential. If that temperature is lower than the metal melting temperature then the particles fusion is impossible. In that case the products being formed have irregular shape and represent binder substance subjected to incomplete gasification with incorporated metal particles. That simulation takes place, for example, in burning of DBSP propellants [2].

In case of hard-to-gasify binder, due to its burning out principally in the places of the binder and oxidizer contact there seems possible a release of binder and initial metal fuel fragments into gas phase, i.e., the formation of first type agglomerates. In the gas phase the pyrolysis of binder takes place and a possibility for particles to ignite and interact arises.

In the work [5] in the framework of justificating the "pocket" type mechanism of agglomeration it is assumed that all particles of initial metal fuel in the propellant contact each other. When the combustion wave propagates the contact bridges between particles are set up and they obstruct the release of particles into gas phase. As soon as AP particles appear ("the pocket" is worked out) the bonds between agglomerating particles and condensed phase of burning propellant are broken and a particle produced as a result of fusion of all particles in the "pocket" is fed into the gas phase.

It is pointed out [9] that in case of binder melting an additional factor is revolved which contributes to relating the particles in the surface layer of burning propellant and to setting up contacts between particles - the effect of capillary forces.

The results obtained in number of works [11,15, and others] give grounds to a consideration that the agglomerating particles are burning. That circumstance leads one to look differently at the conditions under which the agglomeration process is going on. In fact, when metal particles are ignited they melt (metal and oxide melt). Thus, the ambient temperature is not the only criterium of particle fusion possibility. The surface layer should possess a number of specific properties which ensure that high temperature particles are retained. In a number of works [12-14, 19, and others] a suggestion has been made that specific structures are being formed in the surface layer. Burning of agglomerating particles should result in changes of agglomerates properties.

### C. Effect of propellants composition and their burning conditions on dispersity and quantity of agglomerates.

The agglomeration is one of manifestations of SRP burning process and it is quite natural that characteristics of the agglomeration process depend on the propellant composition and burning conditions. When speaking about the effect of the propellant composition we should distinguish the following: - dispersity and content of dispersed oxidizer (DO) and MF; - type of DO, MF, binder.

Currently it seems to be generally accepted that the oxidizer dispersity exerts an extremely essential influence on the agglomeration process characteristics [2,5 and others]. Besides, the decrease in DO dispersity leads to an increase in the agglomerate size. In the works of V.G.Grigoryev [5,20,33] devoted to systematic investigation of the propellant

structure effect on the agglomeration process the author concludes that that factor is the decisive one.

In the works [15, 16] the DO dispersivity is shown to produce an effect on the quantity of agglomerates as well, decreasing it simultaneously with decrease in DO particle size.

It is assumed that the increase in the initial MF powder dispersity leads to intensification of the agglomeration process [2,10]. A similar conclusion is made relatively to the MF content [2,10].

The data on special investigations of DO content influence on the agglomerations are not available. It can be supposed that the effect of that factor is of a contradictory nature. It influences both the propellant burning rate and its structure.

It should be stressed that the change in the propellant ingredient content inevitably causes changes in the propellant energy-producing capacity.

As DO there may be used different substances. As a rule, they are perchlorates, nitrates, nitroamines. (At present AP, ammonium nitrate, ADN, HMX are most widely used). According to the results obtained in the published works it can be assumed that the effect of DO substance on the agglomeration process is due to the following facts:

- effect on propellant burn rate;
- possibility of formation of melted layer on the burning propellant surface;
- change in properties of burning propellant surface layer.

As a rule, it is thought that an increase in the propellant rate leads to a decrease in agglomeration intensity [2]. Universal applicability of the like assertion is questioned by the results of the work [9]. The date obtained in the works [9, 31] show that the formation of DO substance in melted state increases mass-medium diameter of agglomerates by 2-3 times. In the works [13, 15-16] the change in the surface layer properties is shown to result in transformation of the agglomeration mechanisms. It is obvious that a change of MF type should influence the agglomeration process characteristics. (In the works [9, 31] it is shown that substitution of aluminum with magnesium leads to a decrease in agglomerate size). However, it should be noted that both currently used and perspective SRP are the propellants which use aluminum as a MF.

The effect of the binder properties on the agglomeration is related [2], as arule, to the ratio of carbon and easy-to-gasify elements contained in the binder. And for the propellants with moderate content of MF (up to 25%) an increase in carbon content is considered to be a factor contributing to the agglomerate size growth [9, 31]. For the propellants with high content of MF the inverse effect is supposed to take place [9, 31].

Among the conditions of burning it is expedient to single out the pressure in the combustion chamber, character of gas-phase combustion products flow, magnitude and direction of the overload.

Most of the published to date works indicate that the pressure increase is accompanied by the agglomerate size decrease [2 and others]. The given effect is explained by the dependence of the propellant burning rate on the pressure under condition that the burning rate increase is a factor of unconditional decrease of agglomeration intensity. At the same time in the works [5,20] for a rather wide range of propellants it was found that the

agglomerate dispersity doesn't depend on the pressure. For propellants with high content of MF (more than 25% by mass) the complex character of such a dependence has been determined [9, 31]. The pressure increase may be accompanied by both an increase or a decrease in the agglomerate dispersity. In the works [12, 15] it is shown that similar effects may take place in combustion of propellants with lesser MF content as well. Taking into account that the agglomeration process occurs in the surface layer of the burning propellant it may be supposed that the character of the gas flow pass the propellant surface, primarily the longitudinal component of the gas flow velocity influence the agglomerate properties. In the works [2, 27, 28] the effect of the longitudinal component of the gas flow velocity has been experimentally confirmed. The found dependence of the agglomerate size on gas flow velocity has a complex character [2]. Initially the size grows with an increase in velocity, then decreases. Speaking of the effect of the gas dynamic environment on the agglomeration process it is necessary to underline the following: such an effect is possible in the case when the longitudinal component of the gas flow velocity is more or at least, commensurable to the perpendicular component at distances from the burning propellant surface comparable to the size of the particles which are growing bigger. The realization of that condition is considerably influenced by the dimensions of the charge. For big-size engines that condition, as a rule, can't be realized.

The number of experimental works devoted to investigation of the effect of magnitude and direction of overloads on the agglomeration is small. There have been conducted a number of works [22-26] investigating burning rate evolution under effect of overloads where the effect of overloads is related, to some or other extent, to the behavior of condensed products in the surface layer and close to burning propellant surface. It may be considered generally acknowledged that perpendicular pressuring down overloads contribute to retaining the condensed products on the surface of burning propellant which in the limiting case leads to formation of a liquid layer at that surface.

In the work of V.L.Dinks and D.A.Balvin an attempt was made to determine the quantitative relationship between the overload magnitude and agglomerate dispersity. It was shown that the character of that dependence is determined by the properties of oxidizer and initial metal powder. On the whole, in all the cited works devoted to investigation of overload effect mainly the qualitative characteristics are studied.

### **1.2. Formation of highly dispersed oxide (HDO).**

At present it is commonly acknowledged that the flow of CCP, even close to the burning propellant surface, consists of both the agglomerates and HDO particles. If the size of agglomerates may reach hundreds and even thousands micrometers, the HDO particle size is on the order of 1  $\mu\text{m}$ . No works where the HDO dispersity has been investigated under the mentioned conditions came to the knowledge of the present paper authors. It may be supposed that the main source of HDO formation close to the burning propellant surface is the metal not involved in the agglomeration.

A number of works contains data on HDO properties in the ultimate products of propellant combustion [39-41 and others]. It is pointed out that the HDO dispersity depends on propellant properties and pressure in the chamber, the mass-medium diameter of particles being on the range of 2-5  $\mu\text{m}$ . However, since under the given conditions the HDO formation occurs during burning of both the non-agglomerating metal and the metal incorporated in the

agglomerates, then the information supplied in the mentioned works can't be readily used to characterize HDO in the area close to the burning propellant surface.

### **1.3.Numerical modeling of CCP formation close to the burning propellant surface.**

Modeling of CCP formation as a result of the propellant burning boils down, as a rule, to the agglomeration modeling. Since the discovery of the agglomeration phenomenon a number of attempts to model either the given phenomenon as a whole, or its separate manifestations have been made [29-37]. The analysis of the developed models indicates that they don't provide the prediction of agglomerate characteristics with accuracy meeting the practical purposes. Besides, typical of those works is incomplete description of the process which leaves a number of agglomerate parameters undefinable. The use of non-physical or contradictory to experimental data concepts is inherent in some models. The above-mentioned circumstances are not only due to the evident problems of modeling the process in the surface layer of the burning propellant, but probably for the most part because of the incomplete and sometimes contradictory nature of the available experimental material.

### **1.4. Formulating the problem of investigation.**

The conducted analysis of the literature sources gives grounds to the conclusion that the study of CCP formation process taking place close to the burning propellant surface should be directed primarily at obtaining high-quality experimental data since the insufficient amount of them is just the factor restraining the understanding of the processes principle in evolution of MF as a propellant ingredient. To obtain the reliable data the investigation is expected to answer the following requirements:

- completeness of parameters to be registered;
- systematic character;
- availability of statistic data in sufficient amount.

It is well known that changing the DO dispersity is one of the most powerful "tools" to influence the agglomeration process. Therefore within the framework of the present investigation it was suggested to determine the characteristics of CCP close to the burning propellant surface as a function of DO particle size at various pressure levels. It was anticipated that the chemical composition of the investigated propellant will stay the same, and the investigation will consider both the agglomerates and HDO. AP was chosen as it is the most common DO.

### **1.5.Characteristics of propellants.**

The propellant compositions on the basis of isoprene rubber as a fuel-binder and ammonium perchlorate as an oxidizer have been chosen for investigation in the present work. The propellants have equal percentage content of components and differ only in the oxidizer dispersity. Mass contents of components in the propellants are given in Table 1.1. Aluminum is contained in the propellant compositions as powder of spherical particles with diameter of up to 50  $\mu\text{m}$  distributed into four fractions: 0-10 $\mu\text{m}$  (67% by mass), 10-20 $\mu\text{m}$  (16%), 20-30 $\mu\text{m}$  (9%), and 30-50 $\mu\text{m}$  (8%).

**Table 1.1**

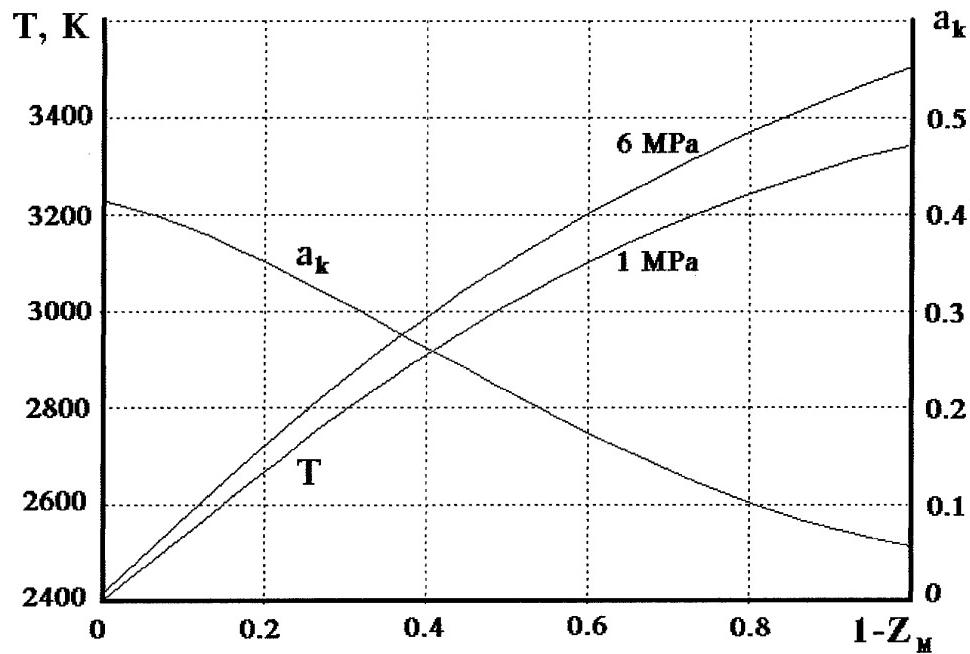
<b>Component</b>	<b>Aluminum</b>	<b>Ammonium Perchlorate <math>\text{NH}_4\text{ClO}_4</math></b>	<b>Isoprene Rubber <math>-\text{CH}_2 - \underset{\text{I}}{\text{C}} = \text{CH} - \text{CH}_2 -</math> C</b>	<b>Additives</b>	<b>SAM</b>	<b>Oil <math>\text{C}_{19}\text{H}_{35}</math></b>
<b>Content by mass, %</b>	24	64	2.6	0.3	0.1	9

To formulate the propellant compositions four fractions of the AP particles are used: the first fraction contains particles with diameter of about  $1\mu\text{m}$ , the particle size in the second fraction is less than  $50\mu\text{m}$ , the third fraction -  $160\text{-}315\mu\text{m}$ , the fourth fraction -  $400\text{-}600\mu\text{m}$ . The mentioned AP fractions are contained in corresponding propellant compositions in proportions given in Table 1.2. Thus, propellant #1 contains AP fractions #1 and #2 in 50% : 50% proportion. Propellant #2 contains only AP fraction #2. Propellant #3 has AP fractions #2 and #3 in 40% : 60% proportion. Propellant composition #4 includes only AP fraction #3, and propellant #5 - only fraction #4. An attempt was made to produce a propellant composition containing only ultra dispersed AP (fraction #1) but it was found impossible to ensure required mechanical properties of propellant samples, namely, their strength and elasticity.

**Table 1.2**

<b>Propellant</b>	<b>#1</b>	<b>#2</b>	<b>#3</b>	<b>#4</b>	<b>#5</b>
<b>Proportion of AP fraction</b>	Fr.#1-Fr.#2 50%-50%	Fr.#2 100%	Fr.#2-Fr.#3 40%-60%	Fr.#3 100%	Fr.#4 100%

Results of thermodynamic analysis for the propellants are presented in Table 1.3 and Fig.1.1, where oxidizing potential ( $a_k$ ), temperature (T), mole mass ( $\mu$ ) of combustion products, and mole fractions of components in combustion products are shown. Parameter  $(1 - Z_m)$  is part of burnt aluminum.



**Figure 1.1** Results of thermodynamic analysis.

P=6.0 MPa

1-Z <sub>m</sub>	0.011	0.500	1.000
T	2412	3103	3520
a <sub>k</sub>	0.407	0.224	0.056
μ	0.03133	0,02930	0.02707
H <sub>2</sub> O	0.33953	0.19711	0.04854
CO <sub>2</sub>	0.06764	0.01396	0.00144
CO	0.20468	0,24065	0.23382
HCl	0,16967	0,15021	0.08930
H <sub>2</sub>	0,14615	0,23887	0.36557
N <sub>2</sub>	0,08512	0,07968	0.07365
NO	0.00000	0,00022	0.00014
OH	0.00006	0,00423	0.00319
Cl <sub>2</sub>	0.00000	0.00001	0.00000
O <sub>2</sub>	0.00000	0.00002	0.00000
AlCl	0.00000	0.00026	0.02076
AlCl <sub>2</sub>	0.00001	0.00048	0.01516
AlCl <sub>3</sub>	0.00001	0,00173	0.00028
Al <sub>2</sub> O	0.00000	0.00000	0.00011
AlO	0.00000	0.00000	0.00002
C	0.00000	0.00000	0.00000
H	0.00007	0,01146	0.03824
O	0.00000	0.00012	0.00012
N	0.00000	0.00000	0.00000
Cl	0.00007	0,00495	0.00619
Al	0.00000	0.00000	0.00213
Al <sub>2</sub> O <sub>3</sub> <sup>k</sup>	0.00113	0.05614	0.10002

P=1.0 MPa

1-Z <sub>m</sub>	0.011	0.500	1.000
T	2400	3018	3351
a <sub>k</sub>	0.406	0.217	0.055
μ	0,03130	0,02901	0,02655
H <sub>2</sub> O	0.33849	0.19060	0.04825
CO <sub>2</sub>	0.06785	0.01455	0.00178
CO	0.20445	0.23760	0.22896
HCl	0.15888	0.14509	0.08798
H <sub>2</sub>	0.13073	0.23617	0.34439
N <sub>2</sub>	0.08531	0.07883	0.07219
NO	0.00004	0.00035	0.00023
OH	0.00090	0.00722	0.00481
Cl <sub>2</sub>	0.00000	0.00001	0.00000
O <sub>2</sub>	0.00001	0.00006	0.00001
AlCl	0.00000	0.00076	0.02466
AlCl <sub>2</sub>	0.00006	0.00135	0.01044
AlCl <sub>3</sub>	0.00002	0.00006	0.00011
Al <sub>2</sub> O	0.00000	0.00000	0.00160
AlO	0.00000	0.00001	0.00041
C	0.00000	0.00000	0.00000
H	0.00166	0.02184	0.06239
O	0.00001	0.00042	0.00052
N	0.00000	0.00000	0.00001
Cl	0.00158	0.00947	0.01072
Al	0.00000	0.00002	0.00371
Al <sub>2</sub> O <sub>3</sub> <sup>k</sup>	0.00115	0.05567	0.09682

**Table 1.3**

## 2.INVESTIGATION OF AGGLOMERATES

The theory of agglomeration should be developed on the basis of reliable experimental data which must be highly representative and informative. It suggests special requirements to the investigation technique which is used to obtain information on physico-chemical characteristics of the agglomerates. To ensure the optimum combination of representativeness and informativeness as well as to achieve simplicity of realization a particle sampling technique in the process of propellant sample burning in the constant volume bomb (CVB) is used here. Particles of more than 30  $\mu\text{m}$  in size are considered to be agglomerates. According to [11, 15] it can be expected that for the class of propellants comprising the investigated compositions the ignition of the agglomerates occurs before their separation from the propellant burning surface and the agglomerates coming into the gaseous phase are burning in the gas-phase mode.

### **2.1.Investigation technique.**

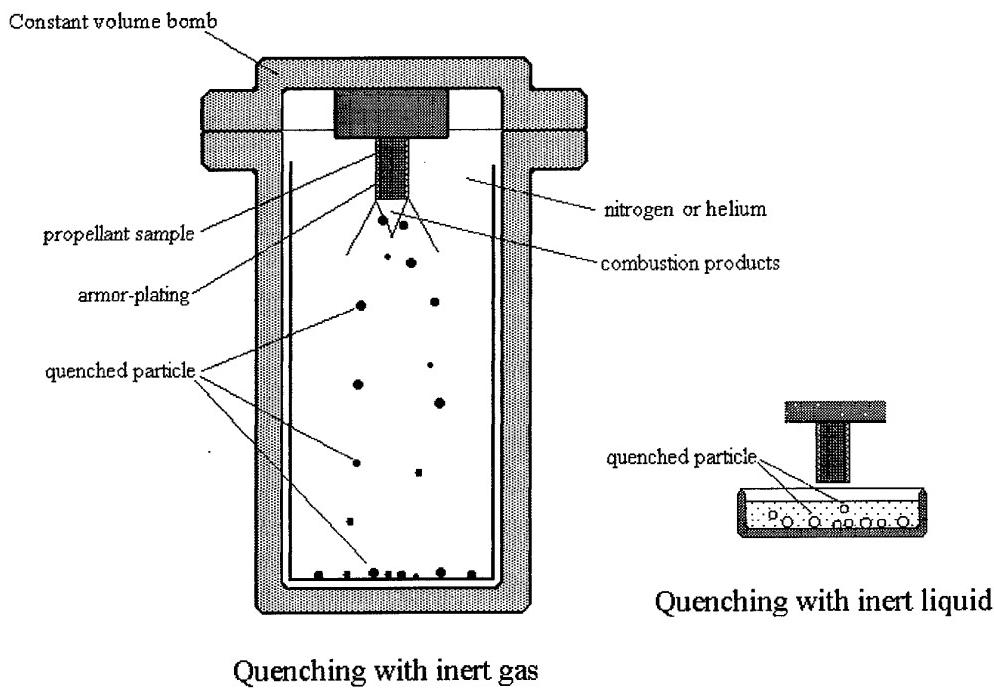
The technique used in investigating the agglomerates is based on their sampling in the process of propellant sample burning in CVB. The general outlay of experiments given in Fig.2.1 consists in the following. Small samples of propellant are being burned in CVB filled with inert gas - helium or nitrogen. The mass of samples does not exceed 2 g which ensures that the pressure in the bomb will increase by not more than 10% during the time of combustion. The shape of samples is a parallelepiped with sides of 5, 5, and 10-20 mm. The side surfaces of the propellant samples are armor-plated which ensures layer-by-layer burning of samples only at one end. The thickness of armor-plating is chosen in such a way as to ensure that the rate of its destruction is close to the burning rate of the propellant composition. The burning of samples takes place on the side with the smallest surface area. Ignition of samples is done with help of a filament heated with electric current. Pressure changes in CVB are registered in the course of experiments which allows to determine the propellant burning rate.

The sampling of agglomerates can be done with help of both inert liquid (alcohol) and inert gas in CVB (helium, nitrogen). In the first case a vessel with inert liquid is placed at required distance from the burning propellant surface. In the second case the quenching and freezing of the agglomerates is done with inert gas in CVB with their subsequent removal from CVB with help of a special container.

In each of the mentioned techniques the sampling of agglomerates is done at some distance from the burning surface. That distance should be the shortest in order to minimize the changes in agglomerate parameters taking place from the moment of agglomerate separation from the propellant surface to the moment of its quenching as a result of agglomerate evolution in the gas phase. In freezing the agglomerates with CVB inert gas the condition mentioned above is ensured by small dimensions of the propellant sample burning surface: 5x5 mm.

In particle sampling with help of inert liquid the location of sampling zone can be readily defined as it corresponds to the liquid surface. When inert gas is used as a "freezing" medium the real zone of particles quenching has a complex spatial form (Fig.2.2). The agglomerate quenching occurs within the boundary layer which is formed when the propellant sample

combustion products flow is mixed with the surrounding stationary inert gas. Theoretical estimate of length of the initial adiabatic part of the flow  $\lambda_i$  gives the following results: for helium -  $\lambda_i=3.6x$ ; for nitrogen -  $\lambda_i=0.4x$ , where  $x$  is the minimum cross - sectional dimension of the propellant sample. The magnitude of  $\lambda_i$  value is a weak function of pressure. To precisely determine the location of the agglomerate quenching zone in the inert gas freezing doesn't seem possible. Therefore in case of the inert gas freezing the sampling conditions for all particles taken as a whole should be averaged, with the agglomerate sampling zone being conventionally imagined as a flat surface A-A. The location of that conventional sampling surface in relation to the sample burning surface (distance  $\lambda$  in Fig.2.2) has been experimentally determined, comparing the results of experiments carried out with help of two different "freezing" techniques: 1 - with help of inert liquid, and 2 - with help of inert gas. To estimate the value of  $\lambda$  the following relations have been obtained: when helium was used as an inert gas  $\lambda=1.2x$ ; where nitrogen -  $\lambda=0.15x$ .

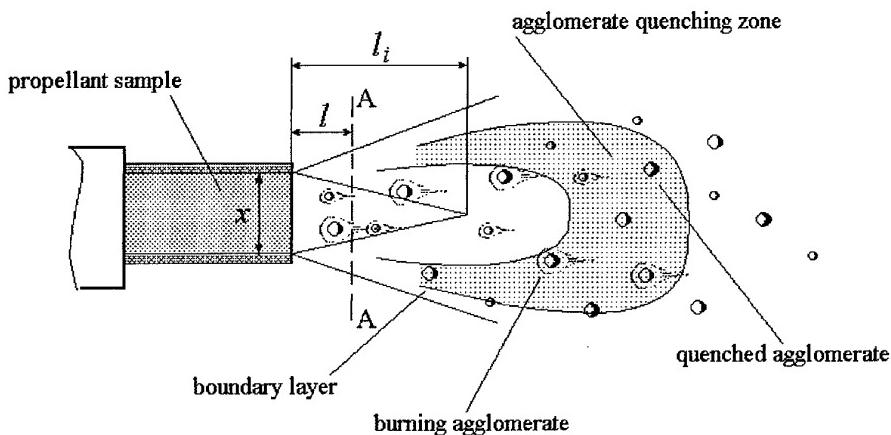


**Figure 2.1** Experimental method

The agglomerate samples are subjected to dispersity and chemical analyses, their structural parameters are determined. The dispersity characteristics are measured with help of microanalyzer "Analyzette 22", FRICH made which ensures measurements of particles distribution by size over the range of 0.1 to 1160  $\mu\text{m}$ .

In analysis of the data obtained with the agglomerate sampling technique a problem arises how to transfer the dispersity analysis data to the high temperature flow conditions. On the one hand, it is necessary to account for the fact that with cooling down the substance density

increases, on the other hand, due to the effect of thermal strains in "freezing" the particles their cracking occurs and, as a result, their density formally decreases. But on the whole, as it had been found before by comparing the result of visualization and sampling the particle sizes determined by mentioned techniques are practically the same. It allows us to make a conclusion that the data obtained in the dispersity analysis of the agglomerate samples are consistent with conditions of the high temperature flow of the propellant combustion products.



**Figure 2.2** Quenching of agglomerates.

Investigation of the agglomerate structure (internal) is done by studying the agglomerate microsections [13], as well as the particle images obtained by means of visualization of the combustion products in the flow. Comparison and analysis of the data obtained with those techniques made possible a conclusion that the agglomerate structure practically doesn't change (doesn't have enough time to change) in the process of the sampling. That is, the structure of the sampled particles corresponds to the one they have in the propellant combustion products flow.

The chemical analysis of samples is aimed to determine contents of aluminum and its oxide in them and is made by means of sample etching in diluted hydrochloric acid with subsequent weighing the remainder. In doing so it should be taken into account that the metal of the agglomerates is subjected to additional oxidation taking place in particles freezing and/or during their contact with air when stored. The additional oxidation considerably distorts the actual characteristics of CCP. The mechanism of that phenomena is the following: in the process of freezing the agglomerates undergo extensive cracking due to high thermal strain effect. On the surfaces of a great number of micro and macro cracks which are being formed therewith the metal oxidizes and produces readily soluble amorphous aluminum oxide (also called "film" oxide). The oxidation process takes place either during the contact of the particles with air, or in the process of freezing during contact with alcohol. The formation of amorphous oxide considerably distorts the real parameters of the agglomerates and it should be accounted for when using the techniques of CCP sampling. The additional oxidation affects about 26% of metal in the agglomerates with degree of the final oxidation being about the same for particle freezing both with inert gas and inert liquid, and for practical purpose it doesn't depend on the agglomerate dispersity. Keeping the samples in storage for a few days doesn't noticeably

increase the oxide content in the agglomerates, but long-term storage (a few months) results in a substantial increase of the additional oxidation of the agglomerate metal, the agglomerates can't stay intact and fall apart.

As a result of the chemical and dispersity analyses the following main quantitative characteristics of the agglomerates are defined:

$Z_m$  - parameter indicating the share of unburned metal in the agglomerate relative to initial aluminum mass in the propellant. Value of  $(1-Z_m)$  characterizes the degree of metal fuel burning out.

$Z_m^{ox}$  - parameter indicating the share of initial metal in the propellant composition used to form oxide in the agglomerates.

$Z_m^a$  - parameter indicating the share of initial metal used to form the agglomerate as a whole.

$\eta$  - mass share of oxide in agglomerate.

$D_{mn}$  - mean diameters of agglomerate samples determined by empirical functions of agglomerate mass distribution density according to their sizes  $f_m(D)$ :

$$D_{mn} = \left\{ \frac{\int_{D_{min}}^{D_{max}} D^{(m-3)} f_m(D) dD}{\int_{D_{min}}^{D_{max}} D^{(n-3)} f_m(D) dD} \right\}^{\frac{1}{m-n}}$$

Where  $D_{min}$  and  $D_{max}$  are minimum and maximum diameters of agglomerates in the samples.

Parameters  $Z_m^a$ ,  $Z_m^{ox}$ ,  $Z_m$  and  $\eta$  are in the following relationships:

$$Z_m^a = Z_m + Z_m^{ox}$$

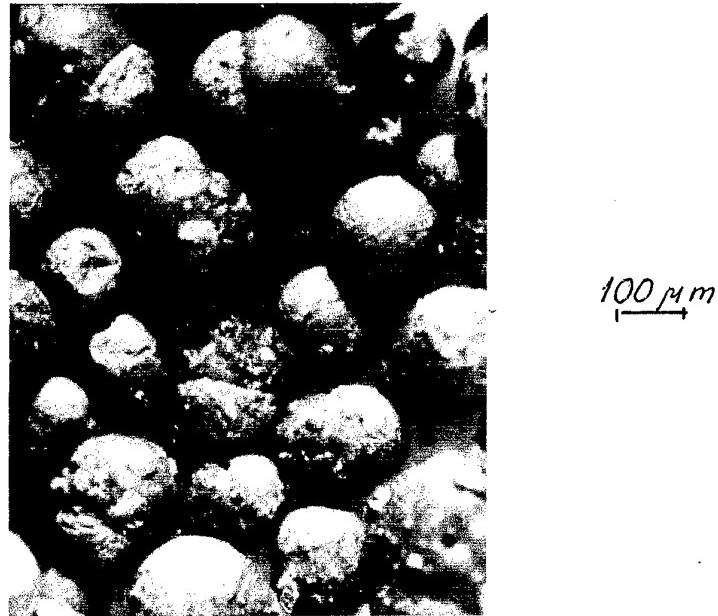
$$Z_m^{ox} = [54/102] [\eta/(1-\eta)] Z_m$$

## 2.2. Investigation results.

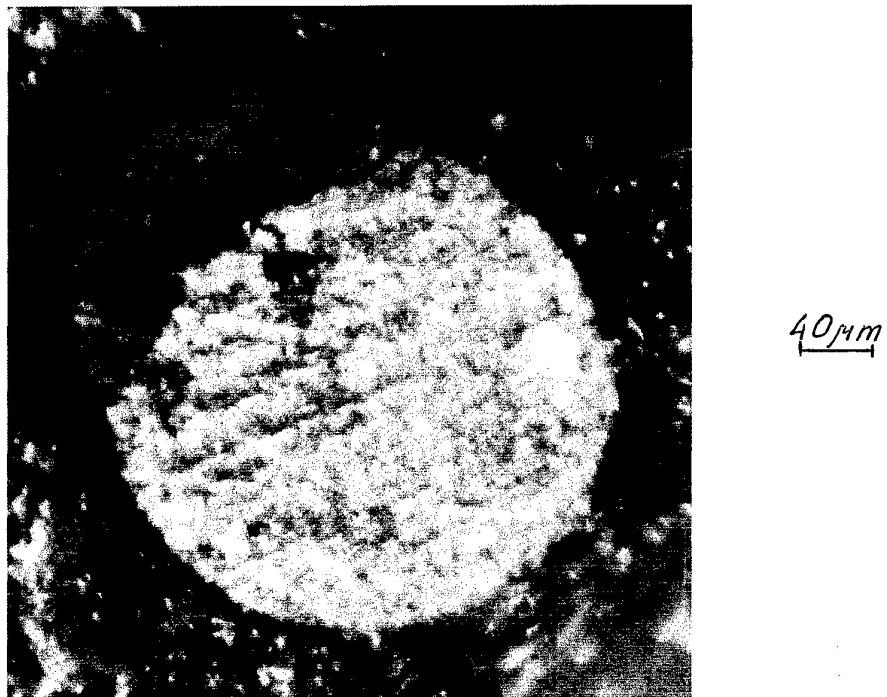
Fig.2.3 shows sampled agglomerates. The analysis of the agglomerate structure has allowed to establish the following: the agglomerate is an aggregate of aluminum and its oxide drops. The oxide forms a "cap" covering partially the metal drop. On the interface of the substances in the agglomerates some gas cavities (bubbles) may be found. The presence of bubbles given evidence of the chemical reaction between aluminum and its oxide running in the agglomerate and producing gaseous reaction products [16, 45]. The photograph of the agglomerate microsection is shown in Fig.2.4.

The shape of agglomerates is characterized by a combination of spherical elements which allows for conclusion that the surface energy of the given system (agglomerate) is of minimum value. That, in turn, makes it possible to view the agglomerates as equilibrium

dispersed system and to assume that the agglomerate structure is completely controlled by the surface tension of the substances it is formed of: aluminum and its oxide both in liquid state.



**Figure 2.3** Agglomerates



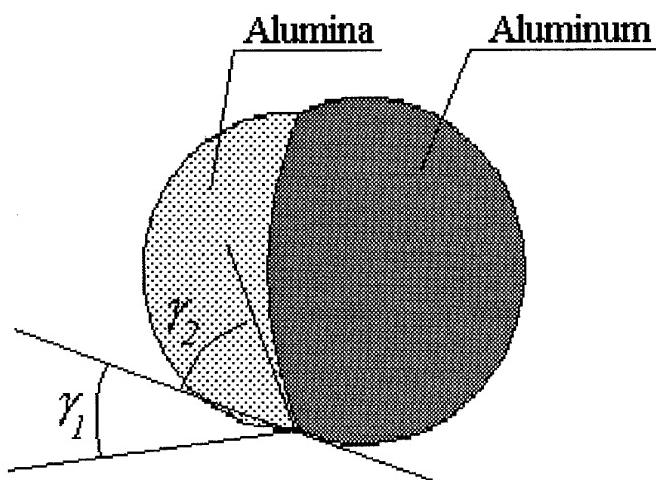
**Figure 2.4** Agglomerate microsection.

The analysis of the agglomerate microsections has allowed to measure the edge angles of wetting  $\gamma_1$  and  $\gamma_2$  (Fig.2.5) as function of the pressure:

at the pressure 6 MPa  $\gamma_1 = 26^\circ$   $\gamma_2 = 41^\circ$

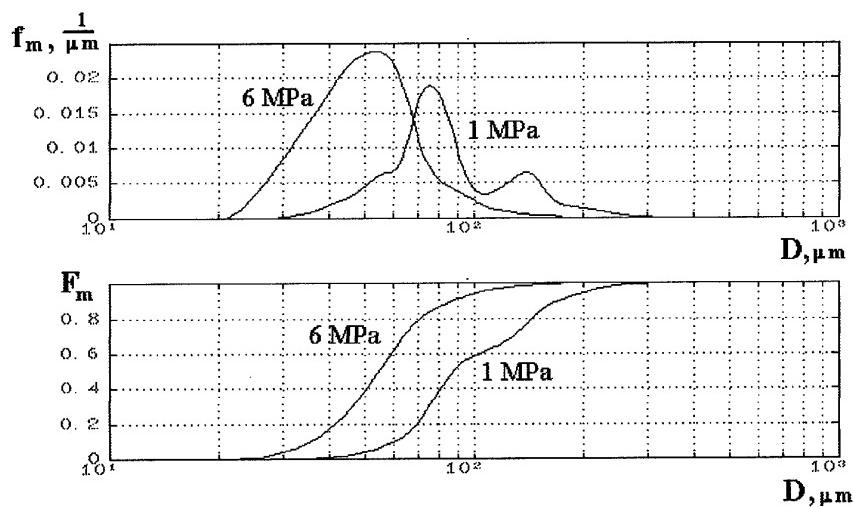
at the pressure 1 MPa  $\gamma_1 = 28^\circ$   $\gamma_2 = 43^\circ$

In measuring  $\gamma_1$  and  $\gamma_2$  it has been taken into account that the agglomerate crosssections are random.

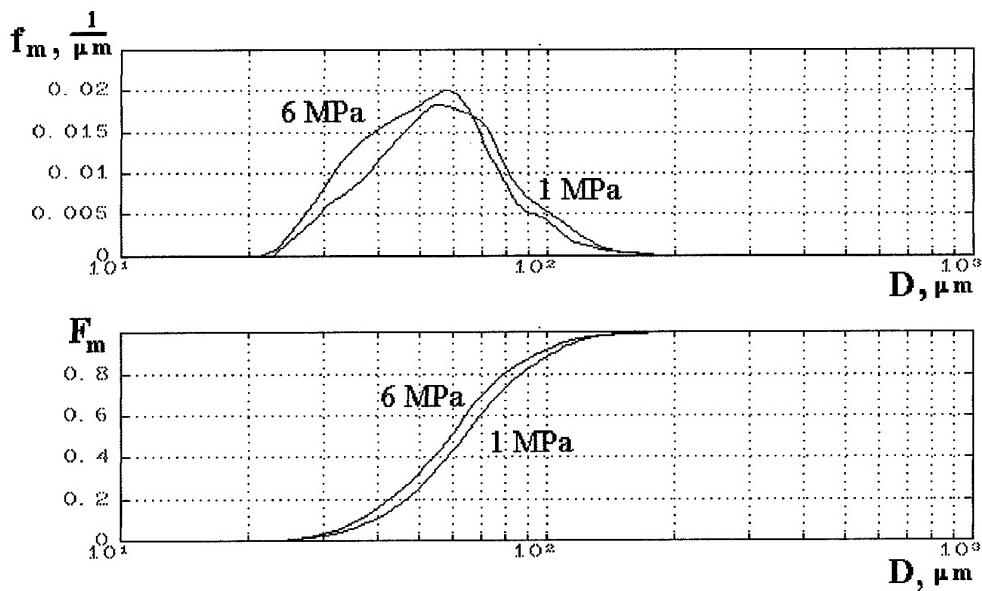


**Figure 2.5** Agglomerate structure

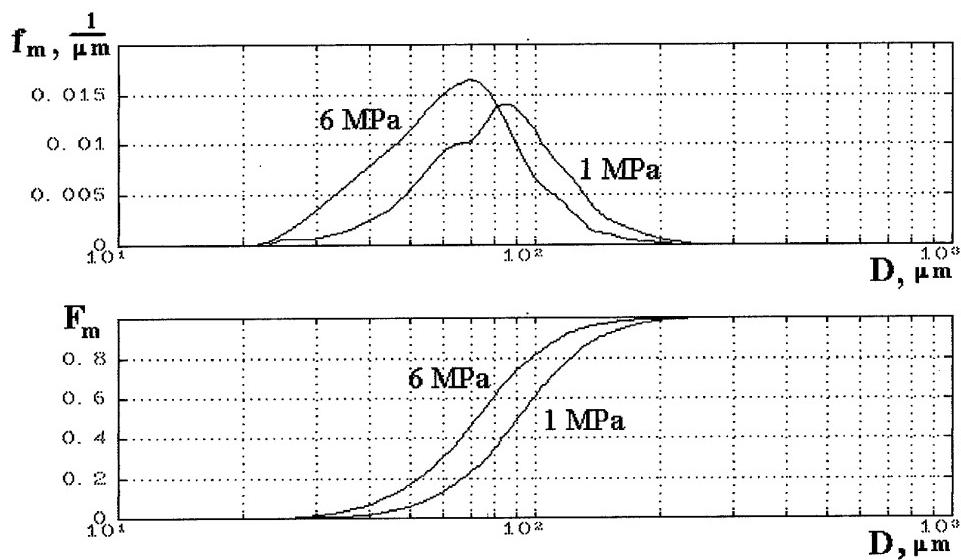
The mass functions of size distribution  $F_m(D)$  and mass functions of size distribution density  $f_m(D)$  for the agglomerates are given in Fig.2.6 - 2.10. A characteristic feature of the distribution density functions is that they can be both unimodal and polymodal.



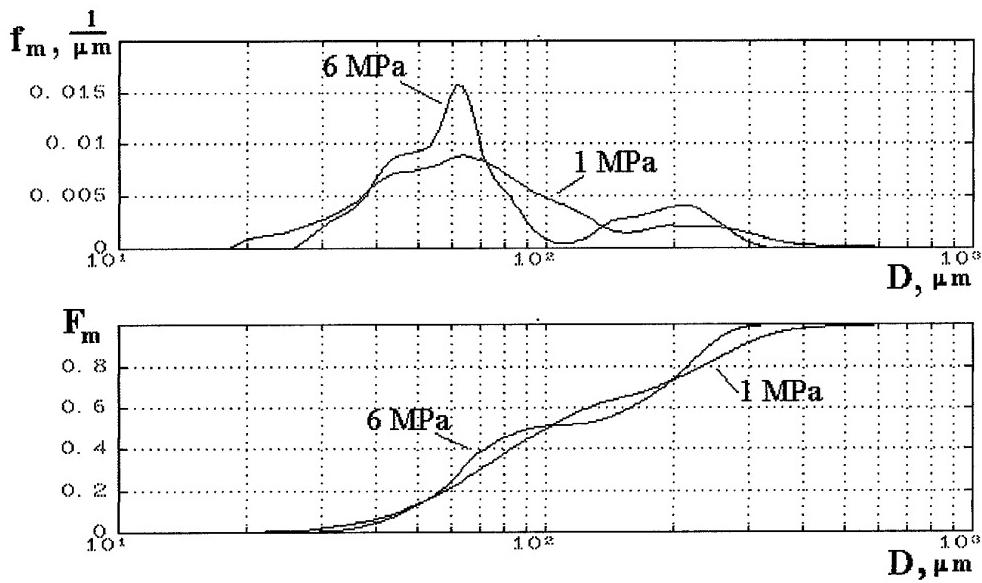
**Figure 2.6** Agglomerate size distribution for Propellant #1.



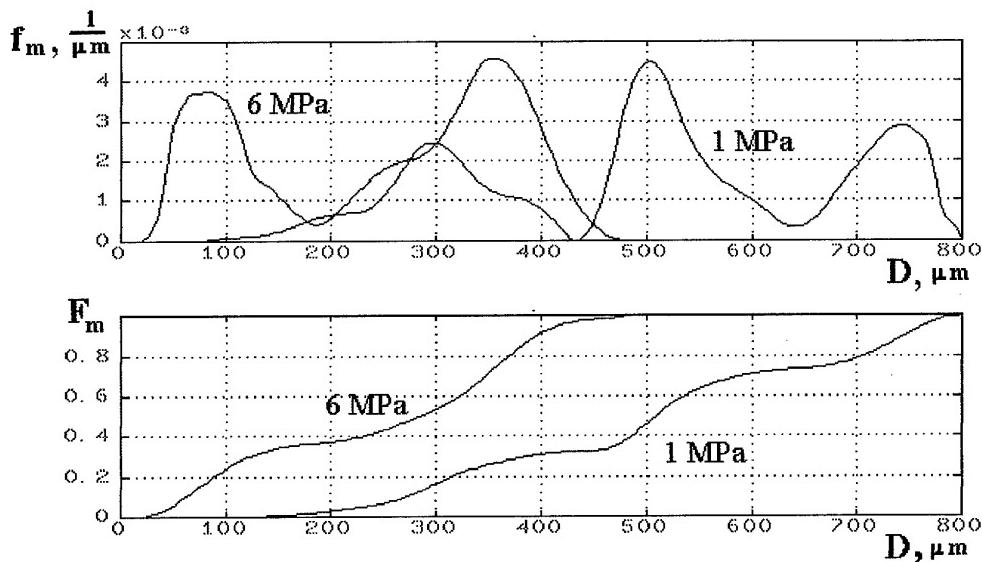
**Figure 2.7** Agglomerate size distribution for Propellant #2.



**Figure 2.8** Agglomerate size distribution for Propellant #3.



**Figure 2.9** Agglomerate size distribution for Propellant #4.



**Figure 2.10** Agglomerate size distribution for Propellant #5.

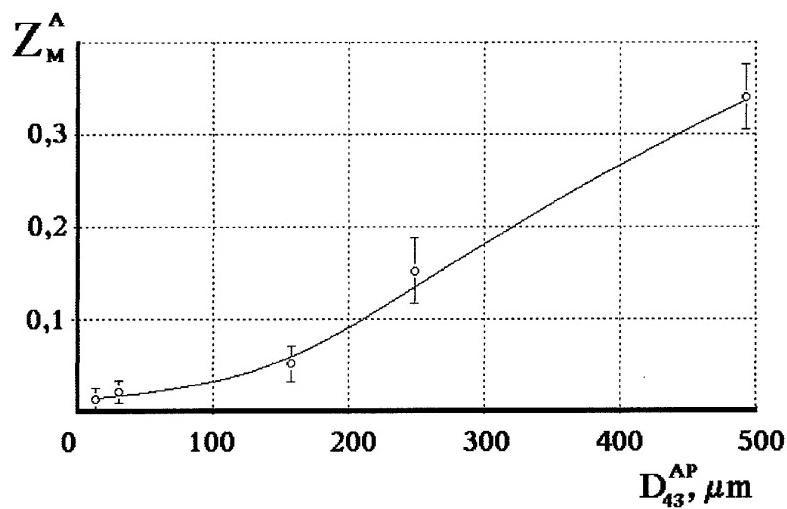
The main quantitative experimental date are presented in Table 2.1 and Fig.2.11 - 2.16 (for the pressure 6MPa), and Table 2.2 and Fig.2.17-2.22 (for the pressure 1MPa). The Figures show dependencies of the main CCP parameters ( $Z_m^a$ ,  $Z_m$ ,  $Z_m^{ox}$ ,  $\eta$ ,  $D_{43}$ ) and propellant burning rate  $U$  on mass-medium diameter of dispersed AP  $D_{43}^{AP}$ . Rather high degree of confidence of the presented data has been ensured by a big volume of the obtained experimental data: for each characteristic not less than 10 experiments have been completed. In Fig. 2.11 - 2.22 the mean values of the corresponding parameters and their confidence intervals for the confidence probability 0.997 are shown.

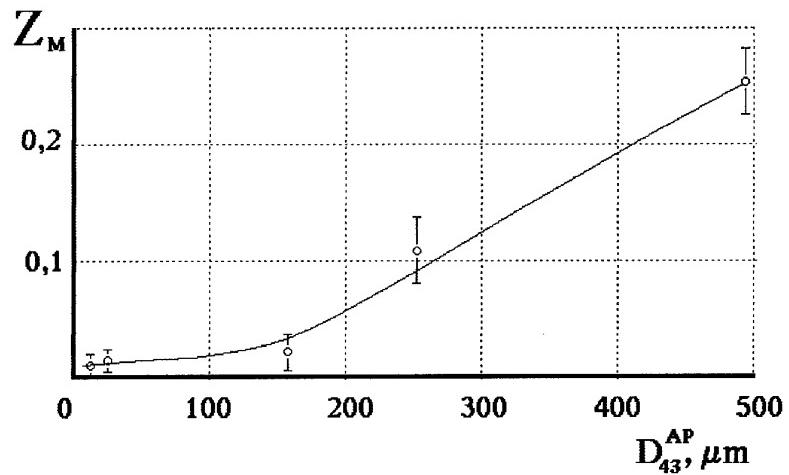
**Table 2.1 (P = 6MPa)**

composition	$Z_m$	$Z_m^{ox}$	$Z_m^a$	$\eta$	$D_{10}, \mu m$	$D_{32}, \mu m$	$D_{43}, \mu m$	$U, mm/sec$
1	0.011	0.002	0.013	0,256	37	51	59	58.4
2	0.015	0.008	0.023	0,502	38	54	62	38.7
3	0.036	0.011	0.047	0,366	45	66	77	28.2
4	0.108	0.045	0.153	0,440	51	87	131	15.0
5	0.254	0.090	0.344	0,401	53	143	250	8.1

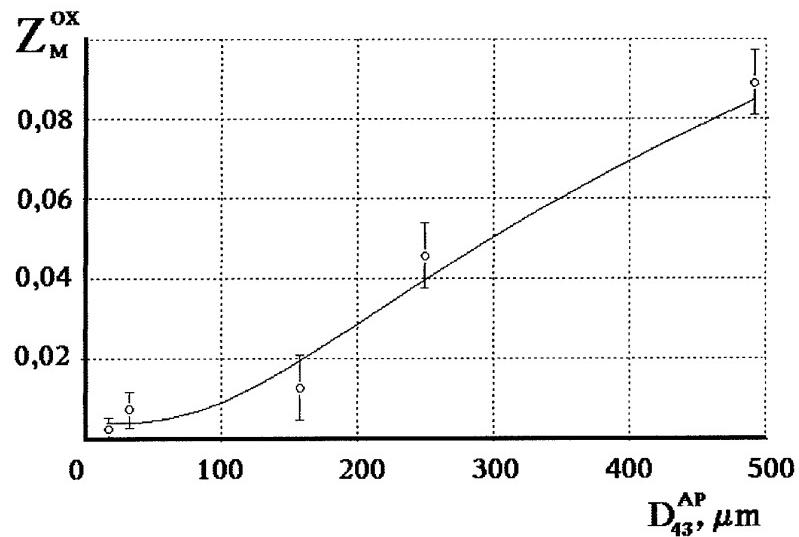
**Table 2.2 (P=1MPa)**

composition	$Z_m$	$Z_m^{ox}$	$Z_m^a$	$\eta$	$D_{10}, \mu m$	$D_{32}, \mu m$	$D_{43}, \mu m$	$U, mm/sec$
1	0.29	0.045	0.335	0,227	67	90	107	34.0
2	0.21	0.021	0.23	0,159	45	59	68	12.0
3	0.32	0.045	0.350	0,210	59	84	98	6.1
4	0.36	0.052	0.409	0,214	44	87	141	6.0
5	0.39	0.063	0.452	0,234	263	430	504	5.9

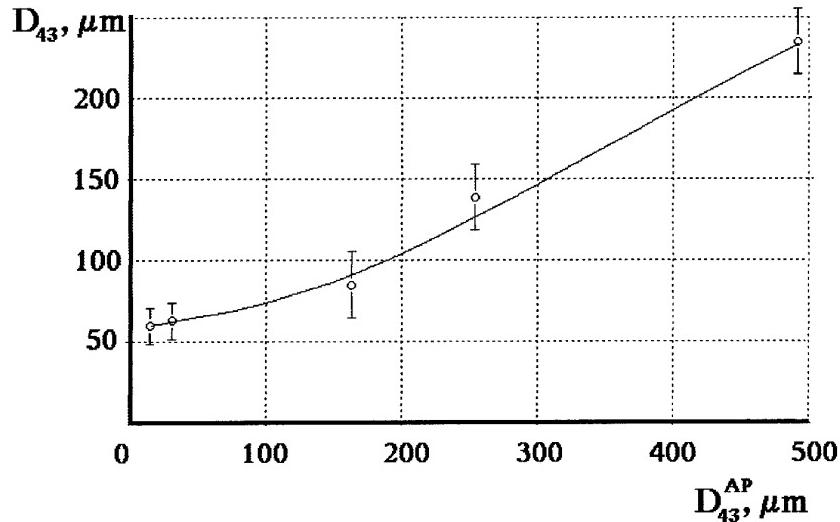
**Figure 2.11** Dependence of  $Z_m^a$  on  $D_{43}^{AP}$ . at high pressure (6MPa).



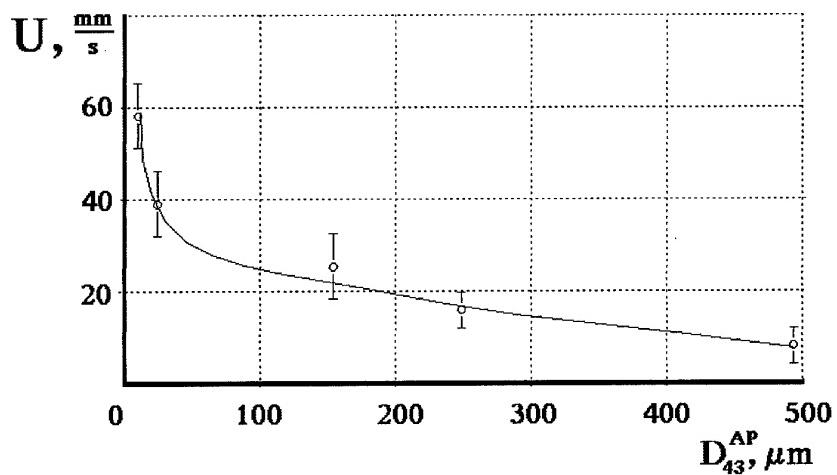
**Figure 2.12** Dependence of  $Z_m$  on  $D_{43}^{AP}$ . at high pressure (6MPa).



**Figure 2.13** Dependence of  $Z_m^{\text{ox}}$  on  $D_{43}^{AP}$ . at high pressure (6MPa).



**Figure 2.14** Dependence of  $D_{43}$  on  $D_{43}^{\text{AP}}$  at high pressure (6 MPa).



**Figure 2.15** Dependence of  $U$  on  $D_{43}^{\text{AP}}$  at high pressure (6 MPa).

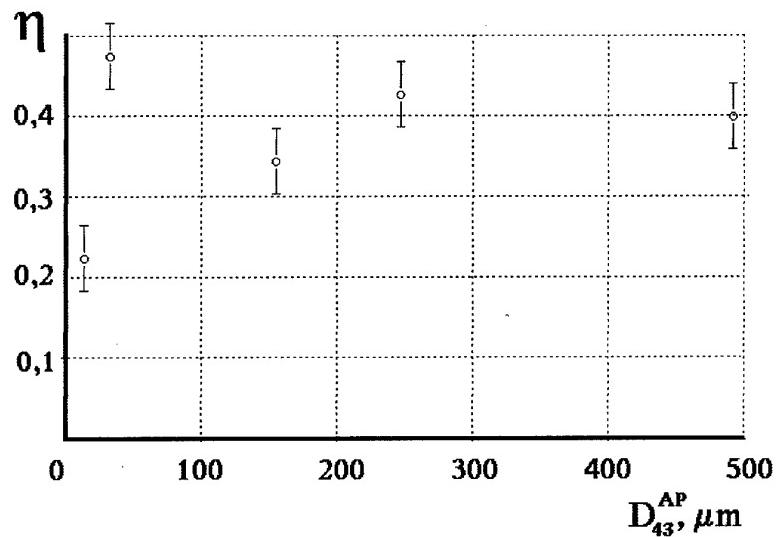


Figure 2.16 Dependence of  $\eta$ ,  $D_{43}^{AP}$  on  $D_{43}^{AP}$ . at high pressure (6MPa).

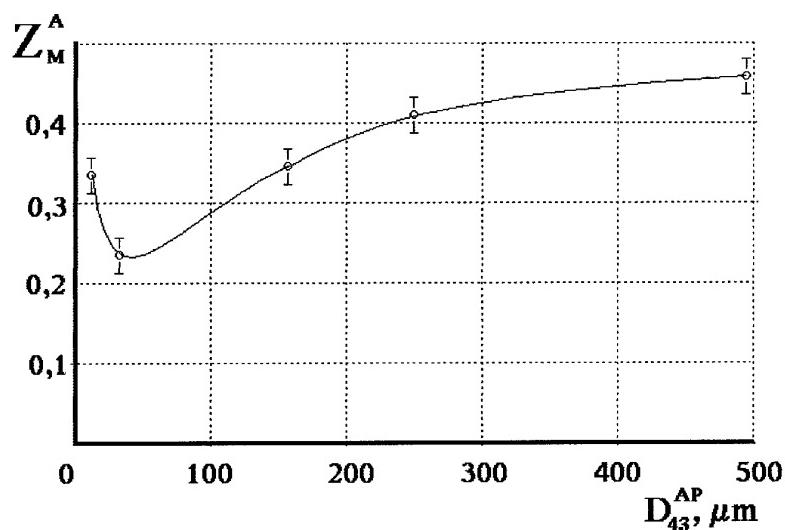
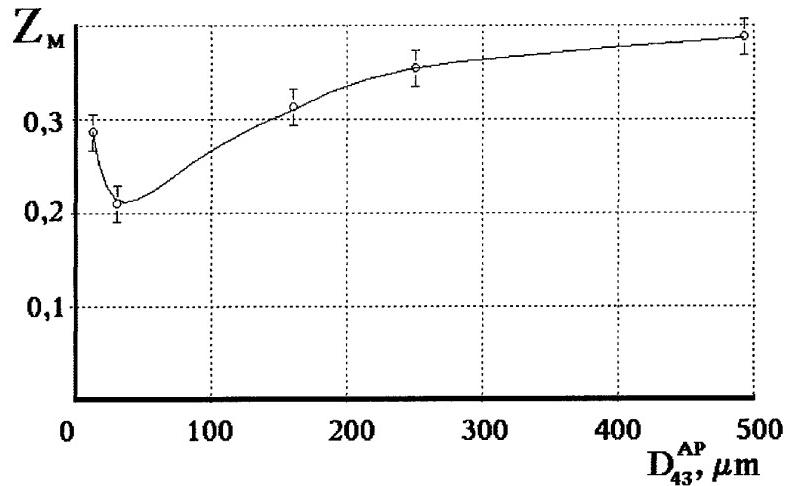
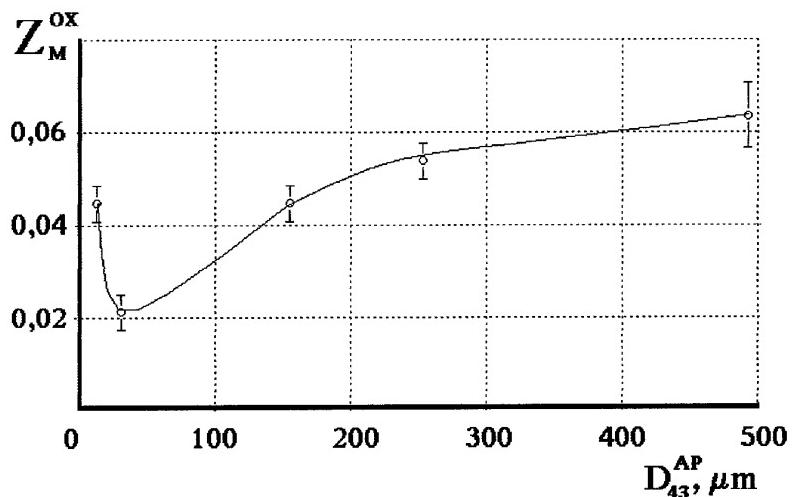


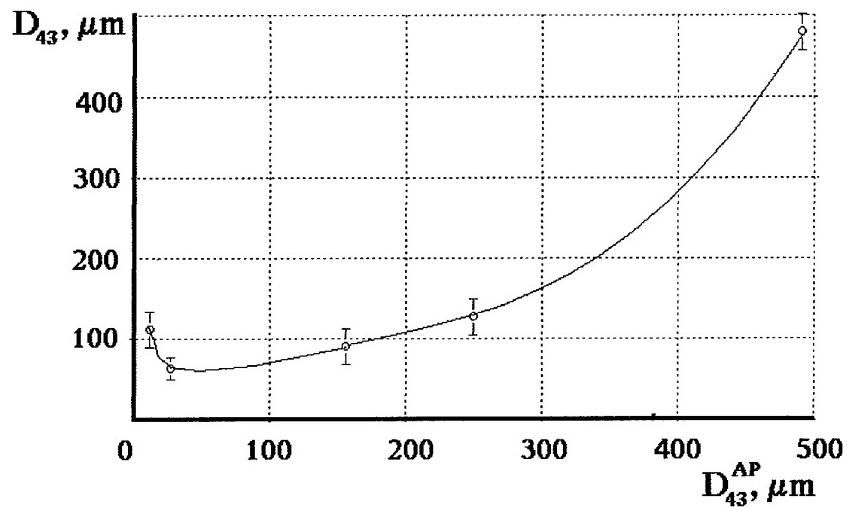
Figure 2.17 Dependence of  $Z_m^a$  on  $D_{43}^{AP}$ . at low pressure (1MPa).



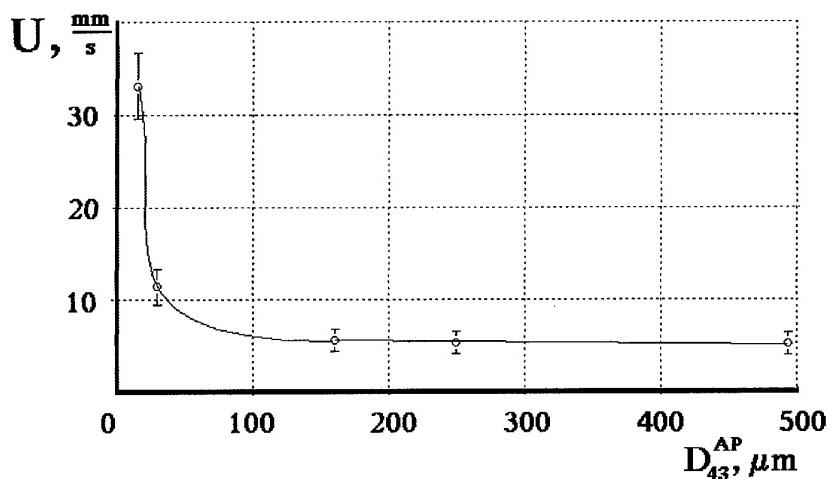
**Figure 2.18** Dependence of  $Z_m$  on  $D_{43}^{AP}$ . at low pressure (1MPa).



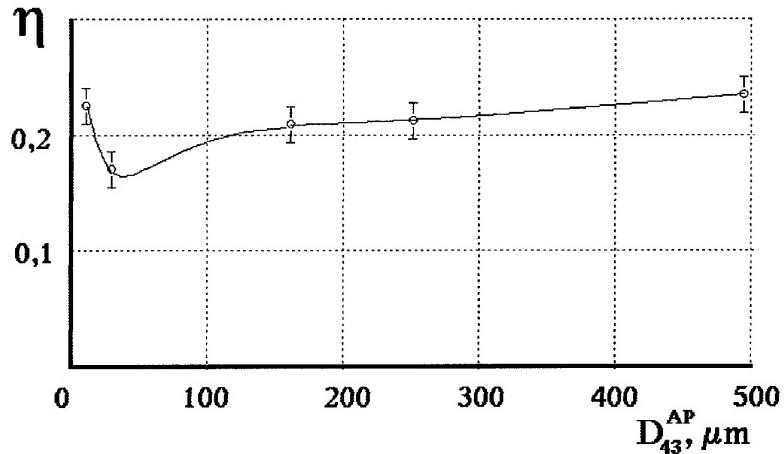
**Figure 2.19** Dependence of  $Z_m^{\text{ox}}$  on  $D_{43}^{AP}$ . at low pressure (1MPa).



**Figure 2.20** Dependence of  $D_{43}$  on  $D_{43}^{AP}$ . at low pressure (1MPa).



**Figure 2.21** Dependence of  $U$  on  $D_{43}^{AP}$ . at low pressure (1MPa).



**Figure 2.22** Dependence of  $\eta$  on  $D_{43}^{AP}$ . at low pressure (1 MPa).

The obtained experimental data show the following nature of the agglomerate parameters dependence on the oxidizer (ammonium perchlorate) dispersity and pressure:

1. At pressure 6 MPa the increase in dispersity of oxidizer (that is decrease of  $D_{43}^{AP}$ ) in propellant (in transition from composition 5 to composition 1) causes monotone decrease of  $Z_m^a$ ,  $Z_m$ ,  $Z_m^{ox}$ , and  $D_{43}$  parameter values. It is significant that the values of  $Z_m^a$  and  $Z_m$  parameters decrease by more than 20 times. At the same time the propellants burning rate increases monotone, and the oxide share in the agglomerates changes insignificantly.
2. At the pressure 1 MPa the character of functions acquires an essential peculiarity. With an increase of the oxidizer dispersity in propellant the values of  $Z_m^a$ ,  $Z_m$ ,  $Z_m^{ox}$ ,  $\eta$ , and  $D_{43}$  parameters first will decrease in a monotone manner (following the transition from composition 5 to composition 2) and much slower than in case with the pressure of 6 MPa, and then (in transition from composition 2 to composition 1) a substantial growth in value is observed for all those parameters. In doing so the propellant combustion rate grows in a monotone manner with an increase in the oxidizer dispersity.

The results of the completed investigations make it possible to conclude that the agglomeration process character depends both on the oxidizer dispersity in propellant and the pressure.

### 3. INVESTIGATION OF HDO

As it was said before it is customary to divide the particles of condensed phase into two fractions: agglomerates and highly dispersed oxides (HDO). The problems of sampling and experimental research of the condensed phase particles, and in particular HDO particles, finding out and studying the effects of factors, which determine the behavior of the HDO formation processes, have been presented to many researchers and the results obtained in their works have been reported in a number of scientific publications [29, 40, 41]. But despite of relatively big number of publications the data on HDO are limited and often contradictory. The more so that in many experiments the mass representativeness of the sampled products have not exceeded 50% which fact calls into question the investigation results due to the little representativeness of the investigated particles. In this connection the development and refining the condensed particles sampling techniques are desirable and represent scientific and practical interests.

In application of the previously developed techniques the particle sampling has been done as a rule, with help of filters [40, 41] but during the sampling large HDO particles precipitate on the chamber bottom that not only hamper the representative sampling but introduce a substantial experimental error into obtained results. Besides, some essential difficulties arise in the particle separation from the filter.

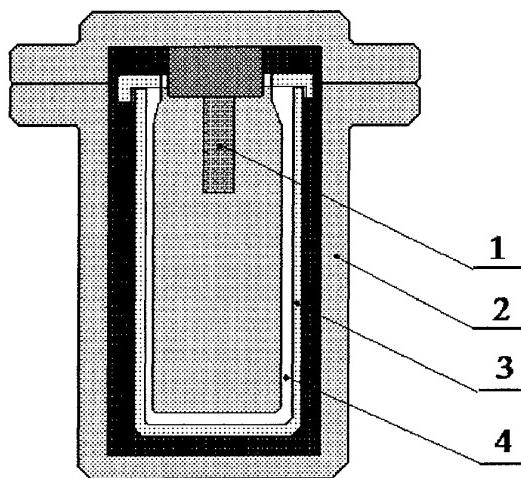
#### 3.1 Technique of HDO experimental investigation.

Within the scope of work on the methods of the HDO particle formation there has been developed a technique for highly dispersed particles sampling which is principally different from all the previously used ones. The developed technique serves for direct determination of HDO particle parameters and is realized with help of contact method of investigation. Within the framework of the technique it is possible to determine the dispersion characteristics, chemical composition of HDO particles, to study the sampled particles under microscope, etc...

The layout of the experimental setup is given in Fig 3.1 .In the constant volume bomb (CVB) 2 a glass vessel 3 is placed in such a way that it takes the maximum possible inside volume of the CVB. It is necessary to avoid possible loss of particles due to their carrying away from the vessel caused by pressure difference in the vessel and CVB during combustion of propellant sample. A layer 4 of ice ~5 mm thick is frozen on the vessel walls to avoid sticking of particles directly to the vessel walls and carrying away of precipitated particles from the CVB when pressure drops. The SRP specimen 1 is placed inside the vessel and ignited with incandescence filament. After combustion of specimen and precipitation of the condensed phase particles on the bottom and inner walls of the vessel, the gas phase products are released from the CVB. Then the particles can be extracted from the liquid by means of evaporation or filtering.

As the condensed propellant combustion products are not only the metal oxidation products but also carbon precipitating as soon due to Boudoir's reaction taking place, the rightful questions is it its presence might distort the obtained experimental data. The chemical analysis of the particle sample of the condensed combustion products has been carried out and it has been found that the carbon content is ~0.5%. It permits us to maintain that the fact of the soot presence is specimen can be neglected. Of special consideration is the question of how long the CVB should remain in the sealed state after combustion of

the SRP specimen, that is, the precipitation the time of the condensed phase particles, taking into account that HDO particle size is  $\sim 1 \mu\text{m}$  and their motion velocity in the gas during precipitation might exert an essential influence on the quantity of sampled particles. The estimate of the spherical particle motion in gas for conditions existing during specimen combustion makes it possible to assess the particle precipitation time and, in particular, shows that all the particles more than  $0.5 \mu\text{m}$  size would precipitate on the vessel bottom over the period of  $\sim 2$  hrs.

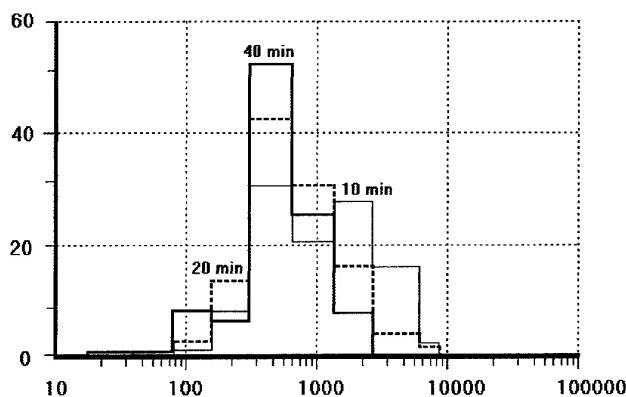


**Figure 3.1** Experimental setup

Previously a number of experiments have been carried out to confirm the efficiency of the given technique. The technique has been tested and improved on the working composition. It has been found that the time of keeping the CVB in the sealed state after the specimen combustion for more than 2 hrs doesn't lead to a considerable increase of the sampled particles mass, it is 99-98% of the estimated and the parameters of the condensed combustion products:  $Z_m$ ,  $Z_m^{\text{ox}}$ ,  $Z_m^{\text{a}}$ , remain the same.

To further investigate the HDO particles they are separated from the agglomerates by means of sifting through a sieve. The selected particles actively agglutinate forming loose coagulants, the process that is determined by the particle surface condition, particle surface charge, etc. To separate the coagulated particles they have been subjected to dispersing in the ultrasound and by adding to the liquid the solution of sodium pyrophosphate (PAV) which hampers the particle agglutination to be repeated and essentially reduces the time of dispersion. The power of the ultrasound impact has been considerably best than the one capable of breaking the integrity of initial particles. It should be noted that the action of the ultrasound on the sampled particles results not only in destruction of coagulants but concomitant with it a repeated coagulation is observed. These phenomena are still poorly studied and can't be precisely predicted. The power of ultrasound impact, ultrasound frequency and dispersion time have been chosen empirically with the aim to obtain HDO particle distribution function as much as possible approximated to a real one, that is, with a minimum quantity of coagulants.

After dispersing the initial dispersion has been diluted with water to get three different concentration and each sample has been analyzed 10 times (10 parallel measurements have been taken) in the particle size analyzer "Coulter 4" for submicronic particles by the dynamic light-diffusion technique. The resolution range of this device is 3  $\mu\text{m}$  ot 10  $\mu\text{m}$ . The printout of the results obtained with help of this device in one of the experiments is presented in Fig 3.2.



**Figure 3.2** Histogram of HDO particles size distribution.

### 3.2 Analysis of experimental data.

Particles identified as HDO particles have a regular spheric form and sizes of tens to thousands of  $\mu\text{m}$  (Fig 3.3). To analyze the regularities of HDO formation close to the burning propellant surface the comparison study of mass representativeness in particles sampling and measurements of dispersity as function of pressure and DO properties was carried out for cases of different composition combustion.

Table 3.1 provides data on mass representativeness of samples at  $P=6.0$  MPa for two compositions (#2 and #5) essentially different in the value of parameter  $Z_m^a$ , as well as for the working composition which has been used for working out the technique. Based on the assumption that in the application of this technique the loss of agglomeration is nil we have measured the fraction of unsampled HDO particles. The experimental results show that a decrease of parameter  $Z_m^a$  gives, as a rule, an increase of this fraction.

**Table 3.1**

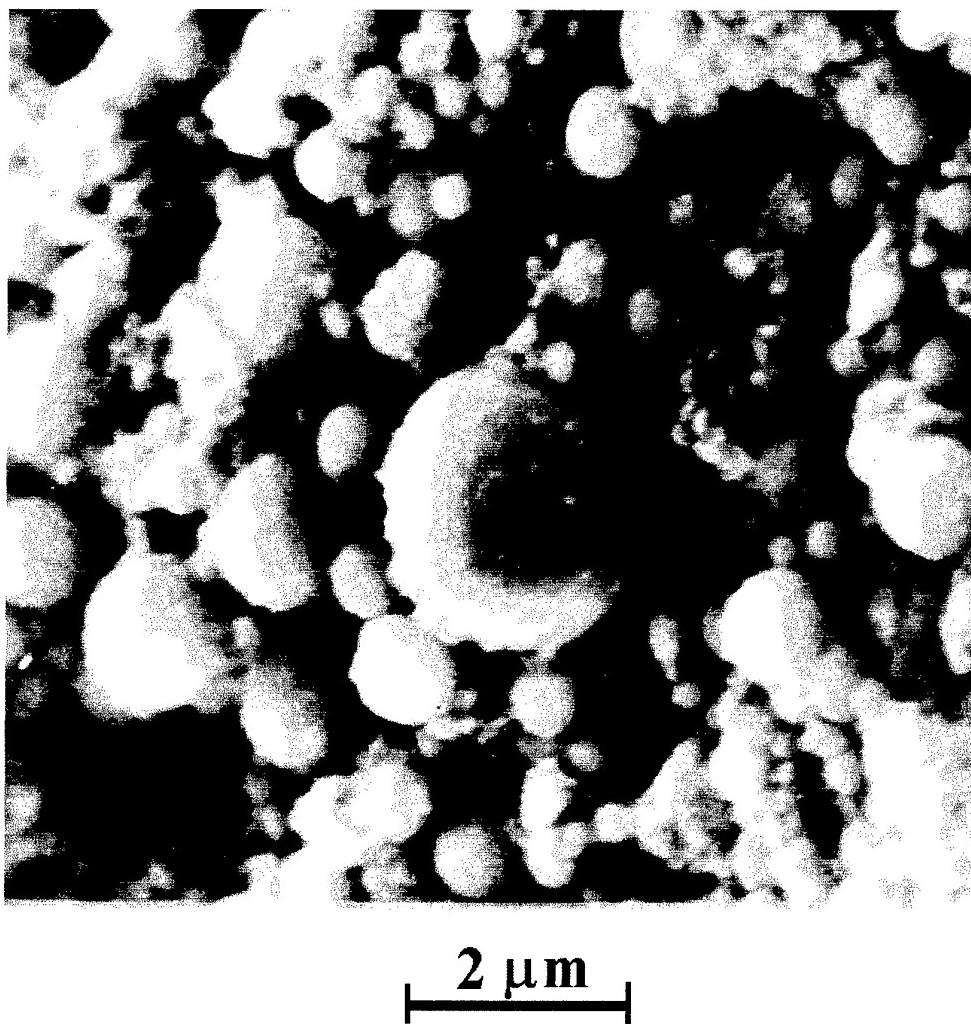
Propellant	$Z_m^{\text{HDO}}$	$D_{43}, \mu\text{m}$	$d_{43}^{\text{HDO}}, \mu\text{m}$	$U, \text{mm/sec}$	$\chi$	$f_{\text{loss}}^{\text{HDO}}$
working	0.36	370	820	5.7	95.3%	13%
# 5	0.64	190	870	8.1	89.5%	16%
# 2	0.97	50	530	38.7	71.0%	30%

$Z_m^{\text{HDO}}$  - fraction of HDO particles in CCP ( $Z_m^{\text{HDO}} = 1 - Z_m^a$ );

$d_{43}^{\text{HDO}}$  - mass - medium diameter of HDO particles;

$\chi$  - part of sampled CCP in the experiment;

$f_{\text{loss}}^{\text{HDO}}$  - part of lossed HDO particles.



**Figure 3.3** HDO particles

Functions  $f_m$  of HDO particle distribution plotted on the basis of the experimentally obtained histograms are given in Fig 3.4.

Apparently, we can speak of two-modal character of these function. The first mode covers the size range of 20-200  $\mu\text{m}$ , the second 300-1000  $\mu\text{m}$ . The fraction of particles forming the second mode is prevailing.

Fig 3.5 gives the dependencies of HDO mass-medium diameter on DO dispersity (composition #) as two pressure levels. With an increase in DO dispersity in switching from composition #1 to composition #5 the HDO dispersity first decreases, then grows. The pressure increase is the factor contributing to a decrease in HDO particle sizes.

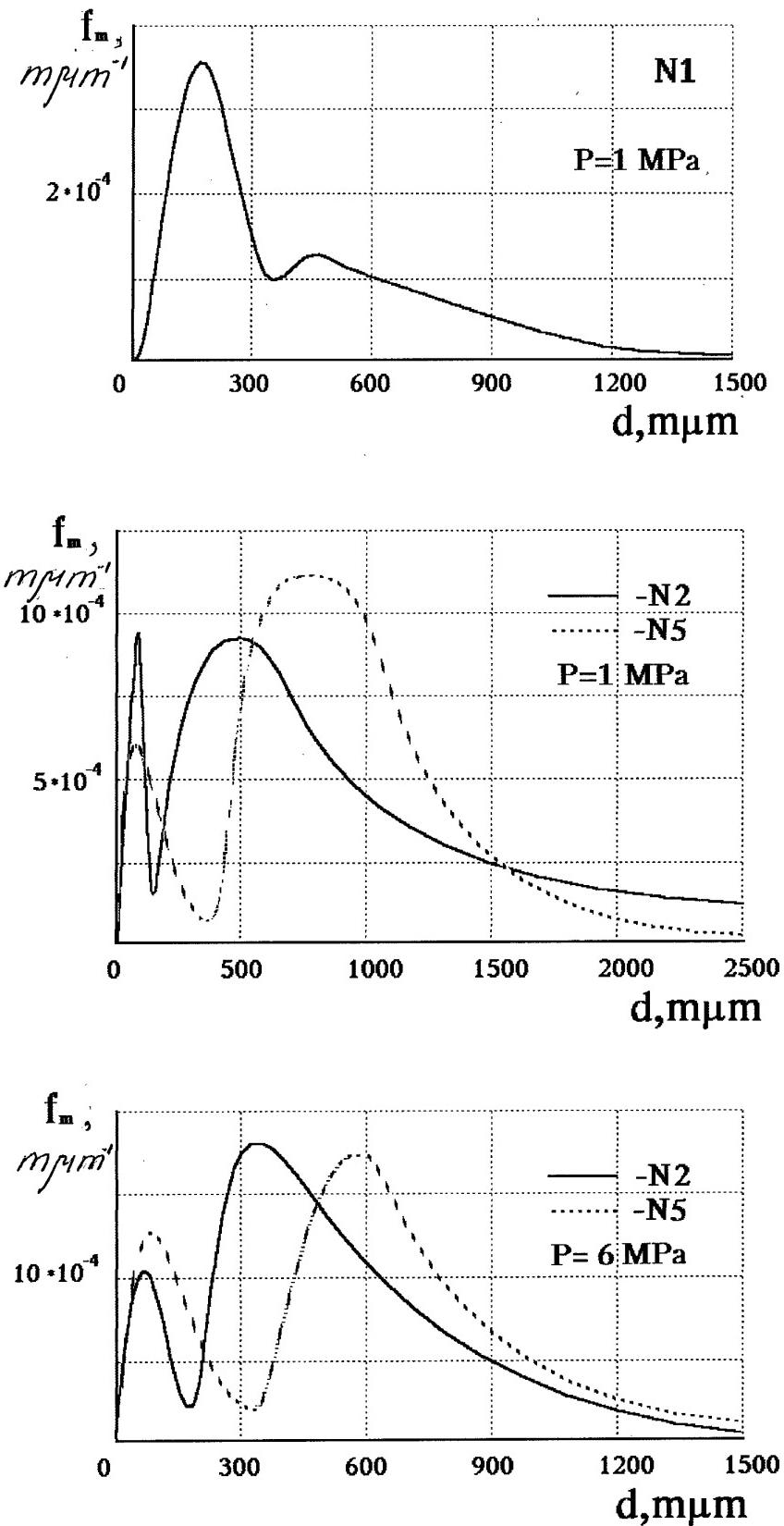
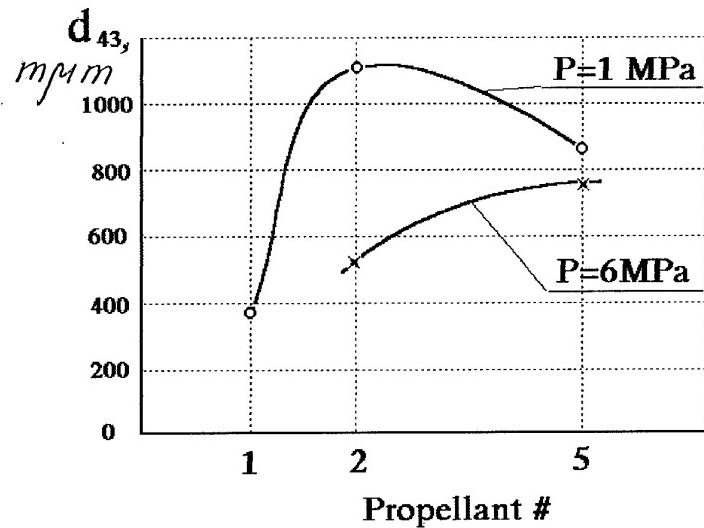


Figure 3.4 HDO particle size distribution.



**Figure 3.5** Dependence of  $d_{43}$  on Propellant number.

#### 4. PHYSICAL CONCEPTS OF CCP FORMATION

The obtained experimental data make it possible to essentially clarify the regularities of CCP formation close to the burning propellant surface.

##### **4.1. Agglomerate formation.**

A vital condition for existence of the agglomeration process is the formation of a specific structure which has been named the skeleton layer (SL) [12-15]. SL is a gas-permeable three-dimensional structure which mainly consists of metal and its oxide, as well as some amount of carbon elements, and which represent the upper portion of the burning propellant surface layer. A characteristic feature of SL is a high coherence of its constituents metal and oxide particles. The SL lower surface may be considered the zone where the degradation of the binder into gas-phase products and solid carbon elements is basically completed. On the SL upper surface (facing the gas phase) the smaller particles are sticking together to produce larger ones which after breaking away form the agglomerate flow.

The present structure provides for realization of the two most important conditions of the agglomeration:

- existence of contact between particles;
- possible retaining of particles (burning ones including !) in the surface layer.

Apparently we can state that MF participating in SL formation takes part in the agglomeration process as well. The physical principles of SL formation are discussed in the work [14]. It is shown that the vital role in SL formation belongs to the carbon skeleton (CS) the evolution of which is determined by the properties of the binder as a polymer and conditions under which its degradation takes place.

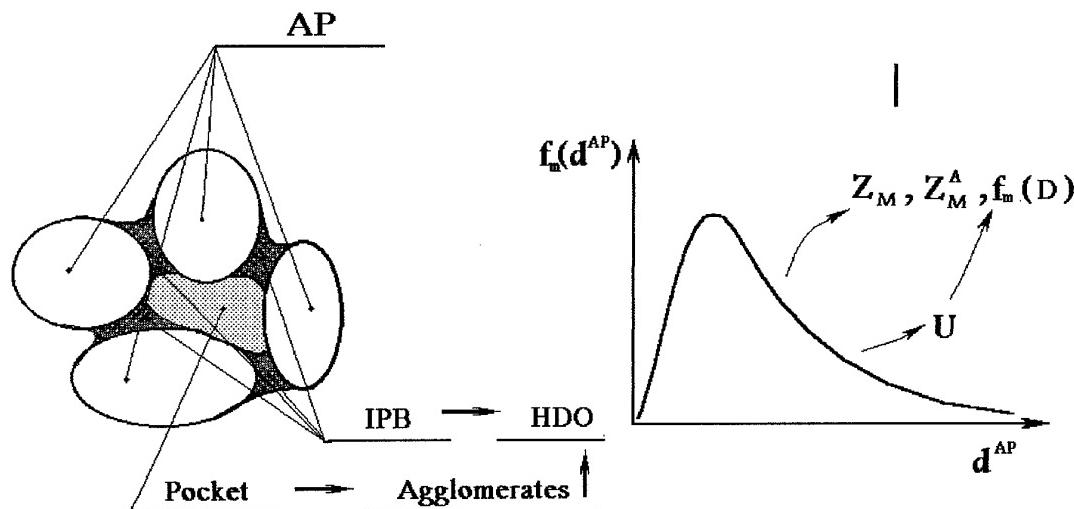
In burning of the composite propellants an essential influence on the CS formation and therefore on the SL is exerted by their structures. For its characterization it is appropriate to use such conceptions as "pocket" and "interpocket bridge" (IPB). Introduction of the conception "pocket" (it goes back to work by Price E.W. and Cohen N. S.), in spite of its apparent conventional nature, has proved to be a fruitful idea in studying the agglomeration. As applied to the real propellant compositions the conditions of "pocket" formation can be defined in the following way:

- DO particles forming the given "pocket" are comparable by their size;
- particular size of the "pocket" is comparable to DO particle size limiting it and considerably exceeds the initial MF particle size.

IPBs represent the cells of the binder-MF composition binding separate "pockets". They can be imagined as interlayers of propellant between DO particles (Fig.4.1). These interlayers burn in the medium rich in oxidizing gases which hamper the formation of the carbon skeleton. The "pockets" burn under characteristically different conditions which make possible the formation of SL. Thus, the proportion of "pockets" and IPBs quantity should exert a considerable influence on the degree of MF involvement in the agglomeration process.

The degree of enlargement of agglomerating particles is determined by the time of their stay on the SL surface. The analysis conducted to study the conditions when particles breaking away from the SL surface [38] allows the conclusion that this time mainly depends on the character of SL heterogeneity and dynamism of the burning process (burn rate). It should be stressed that metal particles participating in the agglomeration process are burning

ones. Immediately after igniting the burning is going on in heterogeneous mode. On reaching some temperature the burning mode changes into gas-phase one. Let us consider how the agglomeration regularities are realized as applied to the investigated compositions. The effect of propellant structure is distinctly seen at low pressure. Under condition that DOs provide for "pocket" formation their dispersity increase leads to an increase of IPB fraction by volume in the propellant mass. The present factor causes a decrease of parameters characterizing MF fraction in the agglomerate composition ( $Z_m^a$ ,  $Z_m$ ,  $Z_m^{ox}$ ) while proceeding from composition #5 to composition #2 (Table 2.2 and Fig. 2.17, 2.18, 2.19). As applied to composition #1 the DO particles due to their small size lose, to a certain extent, the ability to form "pockets" and the propellant undergoes a peculiar sort of "homogenization". (In terms of the structural analysis a homogeneous propellant is one consisting of one "pocket" which has infinitely large size). The result of the above-said for composition #1 is that there take a place an increase of MF fraction participating in the agglomeration in comparison with composition #2 (Table 2.2 and Fig. 2.17, 2.18, 2.19).

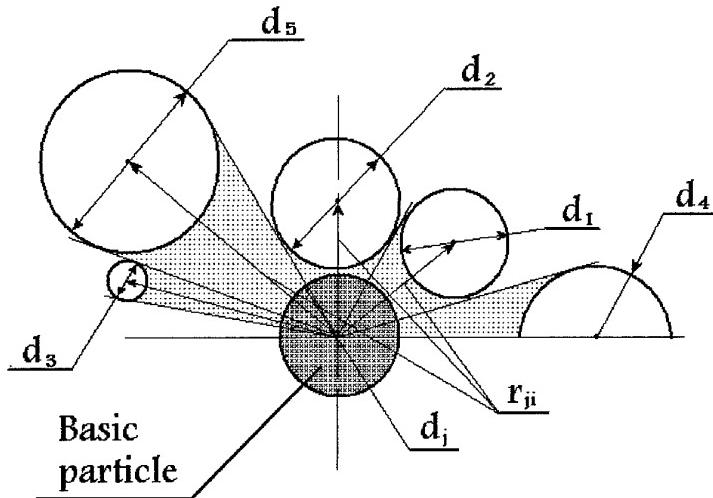


**Figure 4.1** Propellant structure

It seems interesting to compare the obtained results to the results of numerical modeling of the propellant structure which has been done in accordance with the assumptions of work [38]. The modeling is based on the statistical test method which provides for reproduction of the structural formations if the information on the laws governing the distribution of DO particles centers in the propellant and particle size scattering is available. These formations are subjected to the identification procedure to determine the quantity and dispersity of the "pocket" (Fig. 4.2). Given in Table 4.1 values of the "pocket" fraction by volume ( $g_p$ ) in the propellant for different composition may serve as a confirmation of the relation between MF involvement in the agglomeration process and the propellant structure.

**Table 4.1**

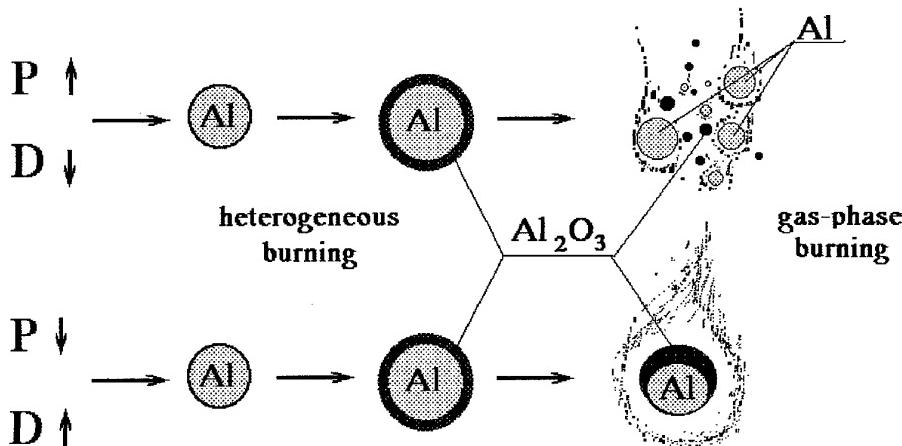
Propellant number	3	4	5
$g_p$	0.26	0.63	0.64



**Figure 4.2** Modeling structure.

The relative content of the oxide in the agglomerates is mainly determined by metal burning in the heterogeneous mode. The obtained results (Table. 2.2) allow us to believe that the metal fraction burning out in this mode increases following the increase in the "pocket" size. As the DO dispersity increases the propellant burn rate and SL heterogeneity changes. The combined effect of these factors is such that in transition from composition #5 to composition #2 the agglomerate dispersity increases (Table 2.2). For composition #1, in spite of the further increase in the propellant burning rate the agglomerate dispersity drops (Table 2.2) that is apparently due to SL heterogeneity decrease.

The pressure rise is a factor contributing to CCP properties change close to the propellant burning surface. And there are some reasons to suppose that not only the absolute values of parameters change, but the CCP formation regularities do too. The only exception is composition #5 (Tables 2.1, 2.2) for which the agglomerate fraction by mass in the flow would remain approximately constant with pressure increase. Only the oxide content in the agglomerates increases which is quite natural if we are to account for a need of increased MF amount burning in the heterogeneous mode to ensure the transition to the gas-phase mode as the pressure increases. For the other compositions the pressure increase leads to a decrease of the agglomerate fraction by mass in the flow. The extent of such a decrease grows as DO dispersity increases. Similar effects in burning of propellants similar to the investigated ones by their properties had also been registered before [11, 42]. As the earlier experiments show their realization is concomitant with a gas-phase temperature rise in the above-the-surface zone as we move away from the propellant burning surface which gives evidence of burning existing in this zone [43]. The analysis of the experimental data (obtained in the present and previous investigations) make it possible to resume that as the pressure grows and metal particle size decreases the probability of realization of the nonstationary effects in transition from heterogeneous mode to gas-phase one (Fig. 4.3) increases. The given effects contribute to the intensification of MF burning in the above-the-surface zone (at distances from the surface not exceeding the position of the sampling zone). For composition #5 the mentioned effects are not essential due to comparatively large size of the agglomerates, for the other compositions they play an important role in CCP formation in the close proximity to the burning propellant surface.



**Figure 4.3** Influence of pressure on combustion mode.

In the process of agglomeration three mechanisms might be realized: "pocket", "prior-to-pocket" and "interpocket" types [12,15]. The first mechanism is characterized by formation of only one agglomerate by the MF of each "pocket" and by the absence of agglomeration parameters dependence on the pressure. When the second mechanism is realized the agglomerating particles leave the SL surface before the "pocket" is worked out. The realization of the third mechanism supposes a possible fusion of particles belonging to different "pocket" ("interpocket" fusion). If the quantities of particles which are formed according to different mechanisms are comparable then the density function of the agglomerate size distribution becomes polymodal. It is shown [12,15] that for propellants similar in properties to the investigated ones at pressures close to the atmospheric it quite probable that the "pocket" mechanism would be dominant. The pressure increase is accompanied by intensification of agglomerate formation following the "prior-to-pocket" or "interpocket" mechanisms, that is, there are two factors in action, one of them contributes to agglomerate dispersity growth, the other - to a decrease. The competition of the described mechanisms of agglomeration when the pressure changes, as well as the realization of the discussed nonstationary effects leading to disappearance of agglomerate small fractions just determine the agglomerate dispersity as a function of the pressure (Table 2.1, 2.2 and Fig. 2.14, 2.20). The obtained results give another confirmation of the fact that the pressure growth might be accompanied by an increase, absence of change or possible decrease in the agglomerate dispersity close to the propellant surface.

#### 4.2. Formation of HDO

The most general concepts allow us to argue that in the burning of aluminum-containing SRP the HDO particles are formed in the course of combustion of the unagglomerating metal and the metal participating in the agglomeration process. (In the present paper it is supposed that the metal particle formed due to the agglomerate fragmentation as a result of the existing non-stationary effects are placed in category of unagglomerating metal.) Close to the burning propellant surface the combustion of the agglomerating metal is comparatively weak which allows us to assume that the first factor effect on the HDO formation is predominant.

We should state that at present the mechanism of the highly-dispersed metal particle combustion in the medium characterized by the presence of fields of temperature, oxidation potential and gas velocities, and noted for high gradients of the corresponding parameters is actually not studied. It is possible to point out some quite obvious specific features of this process: high rates of heat-mass exchange of particles with environment, potential realization of non-stationary effects. It seems unjustified to apply the laws of rather large-size particle combustion, for which quite a lot of experimental data have been obtained, to the situation examined here. It is quite probable that the burning of the unagglomerating metal runs in two combustion modes: heterogeneous and gas-phase, in realization of which the condensed combustion products are formed either on the burning propellant surface or in the gas-phase. The observed two-modality of the HDO particle size distribution density functions (Fig.3.4) is probably the result of this assumption realization. It may be supposed that appearance of the first mode which corresponds to the small-size range is determined by the HDOs formed in the gas phase, and the second - on the particle surfaces. As the probability of the small-size particles missed in sampling in comparison to the large-size ones is higher, then we can suppose that an essential portion of lost particles (Table 3.1) comprises precisely small-size particles; that is, the fraction of particles forming the first mode is somewhat bigger in quantity than the measured. It should be noted that formation of oxide particles of less than 100-150  $\mu\text{m}$  size is a specific feature of the processes taking place under shock-wave stress condition of Al powder when development of the like particles is related to the phenomena occurring in the gas phase [44 and others].

At the present time we can only suppose what is the range of parameters exerting influences on combustion of metal not entering the agglomerates. Among them we should name the propellant burning rate, pressure, quantity of particles participating in burning. But the results of the present investigation enable to assert that the parameters of HDOs close to the burning propellant surface are the individual characteristic of propellant and its burning conditions.

It is necessary to note that HDO dispersity determined within the framework of the present investigation proved to be, on the average, higher in comparison with the results of practically all the previous works. (We remind that in those works the final products of combustion had been examined). This circumstance allows us to assume that in the process of CCP evolution in the gas phase when the formation of the HDO during the agglomerate metal burning and the interaction of the carrier gas phase and the agglomerates [15, 45] take place we can expect a HDO dispersity decrease.

## Conclusion

Within the framework of the present work the properties of CCP close to the burning propellant surface have been examined. The most essential features of the investigation are:

- comprehensive and representative character of the obtained data (subject to investigation is a totality of the condensed products; a wide range of CCP characteristics describing dispersity, chemical composition and particle internal structure are determined);
- systematic character of the experiment conduct which allows us to find out the influence of one factor with others being invariant (to change DO dispersity or the pressure with other parameters of composition and burning conditions remaining unchanged).

In the process of the investigation the following principal scientific results have been obtained:

1. General characteristics of the CCP flow have been determined. It has been shown that it consists of two essentially different types of particles: HDOs and agglomerates. Morphological and chemical properties of these particles have been defined.
2. It has been shown that to characterize the propellant structure it is expedient to use such concepts as "pocket" and "interpocket bridge".
3. The character of DO dispersity and pressure influence on the proportion of agglomerates and HDO particles has been determined. An increase in DO dispersity up to some level determined by "pocket" formation conditions leads to a decrease in the fraction of metal participating in agglomeration. Further dispersity growth ensures an increase of the fraction. The pressure increase is the factor which contributed to the agglomerate transformation relative to HDOs, following the agglomerate dispersity increase, which takes place in close proximity to the burning propellant surface, and therefore decrease the agglomerate fraction in the CCP flow.
4. It is shown that there is a dependence between the fraction of metal participating in agglomeration and the propellant structure. Modeling of the structure allowing for determination of characteristics for various structural formations enables us to predict the degree of metal involvement into agglomeration.
5. The character of the DO particle size influence on the agglomerate dispersity has been determined. It shows itself as a change in the propellant burn rate and "pocket" sizes. An increase in the rate and "pocket" size results in the agglomerate size decrease.
6. It has been shown that the agglomerate formation may involve different mechanisms: "pocket", "prior-to-pocket", and "interpocket" types. Transformation of these mechanisms with pressure change leads to changes in the character of pressure influence on agglomerate dispersity.

7. It has been established that HDO are mainly formed in burning of the metal not participating in the agglomeration. The HDO particle dispersity changes depending on both the pressure and the DO dispersity, that is, its parameters are individual characteristics of the propellant and conditions of its combustion.

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